

Enhancement of Critical Current across Single Grain Boundaries in $\text{YBa}_2\text{Cu}_3\text{O}_x$ and Search for Superconductivity in Alkali Metals

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Abstract

The ability of single grain boundaries in $\text{YBa}_2\text{Cu}_3\text{O}_x$ bicrystalline rings to carry electrical current is found to be significantly enhanced under hydrostatic pressure. Nearly hydrostatic pressures are applied to the alkali metals Li, Na, and K. in a search for superconductivity. Whereas Li becomes superconducting above 20 GPa at temperatures as high as 15 K, no superconductivity was observed above 4 K in Na to 65 GPa nor in K above 4 K to 43.5 GPa or above 1.5 K to 35 GPa.

1 Introduction

The first high pressure experiments on a superconductor were carried out in 1925 by Sizoo and Onnes [1], 14 years after the discovery of the first superconductor [2]. Since then high-pressure investigations have had an important impact on the field. Following the discovery of a new superconductor, one of the first experiments is to determine the pressure dependence of the superconducting transition temperature T_c . If the magnitude of dT_c/dP is large, one can have good hope that higher values of T_c at ambient pressure are possible. In addition, a comparison of the pressure dependences of T_c with those of selected normal state properties provides information regarding the mechanism(s) responsible for the superconductivity, as recently illustrated for MgB_2 , the high- T_c oxides, and the alkali-doped fullerenes [3].

In this paper we give further examples to illustrate how the high-pressure technique can provide vital information and uncover new physics for two completely different classes of superconductors: (1) the high-pressure enhancement of the critical current density J_c across a single grain boundary (GB) in bicrystalline rings of the high- T_c oxide $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO), and (2) pressure-induced superconductivity in the alkali metals. The observation of pressure-induced superconductivity in Li is at odds with the conventional wisdom that metals become more free-electron-like under pressure.

2 Results on YBCO Grain Boundaries

Shortly after the discovery of the high- T_c oxides in 1986 it became clear that the J_c -values for polycrystalline materials not only are vastly inferior to the those obtained in single crystalline samples, but also degrade sharply in a magnetic field [4]. Experiments on epitaxially-grown YBCO thin films demonstrated that this strong degradation in J_c resulted from the presence of grain boundaries in the polycrystals [5]; for adjacent grains with parallel c -axes, J_c was found to decrease roughly exponentially with increasing misorientation angle θ [6]. Pinpointing the mechanisms behind this J_c degradation and developing strategies to enhance J_c to the values needed for many applications have been at the focus of intensive research for many years.

Possible candidates for the J_c degradation include various types of imperfections in or at the GB such as site disorder, lattice strains, and oxygen vacancies [4, 7, 8]. High-pressure experiments may shed some light on these matters by modifying the conditions at the GB in several different ways: (1) reduction of tunneling barrier width, (2) varying the degree of lattice strain, (3) enhancing the degree of oxygen ordering in the GB, in analogy with the well studied pressure-induced oxygen ordering effects in the bulk [9, 10]. The very existence of relaxation effects due to oxygen ordering in the GB would signal that the oxygen sublattice is only partially full and thus capable of accepting further oxygen doping.

Previous ac susceptibility studies on bulk polycrystalline samples of $\text{YBa}_2\text{Cu}_3\text{O}_x$ and $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$ indicated that the bulk J_c was enhanced through pressure, but it was not possible to extract detailed information [11]. Studies of pressure-dependent effects for a single grain boundary are clearly needed. Such experiments have recently become possible with the availability of bicrystalline rings of $\text{YBa}_2\text{Cu}_3\text{O}_x$ with varying misorientation angles θ and oxygen content x [12].

The He-gas pressure cell (Unipress) suitable for hydrostatic pressure studies to 1.4 GPa is shown in Fig. 1. The YBCO bicrystalline ring with typical dimensions 5 mm O.D. x 3 mm I.D. x 1 mm is mounted in the sample holder made of Vespel which is placed in the 7 mm bore of the BeCu pressure cell. An alumina cylinder is positioned above the sample holder to reduce the volume of He in the cell.

Two counterwound pickup coils are used in the ac susceptibility measurement, one positioned around the YBCO ring, the other 2.3 mm below. To vary the temperature over the range 6 - 300 K the pressure cell is placed in the sample tube of a closed-cycle refrigerator (Balzers) with the BeCu capillary tube (3 mm O.D. x 0.3 mm I.D.) exiting out the top and connected to a three-stage He-gas compressor system (Harwood) to 1.4 GPa with a digital manganin gauge. Since primary ac field amplitudes as high as 300 G are required, internal heating effects are avoided by removing the field coil from the pressure cell and placing it outside the tail piece of the cryostat. To ensure full field penetration to the sample, the frequency of the ac field was reduced to 1 Hz. Standard ac susceptibility techniques are used with a SR830 digital lockin amplifier.

In Fig. 2 (left) the real part of the ac susceptibility χ_{ac} is plotted versus tem-

perature for an *ac* field amplitude of 1 G at both ambient and 0.6 GPa hydrostatic pressure. The sample studied is a $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ bicrystalline ring with misorientation angle $\theta = 30^\circ$. At temperatures below 88 K at ambient pressure, the applied flux is not able to penetrate into the ring since the induced current density through the two grain boundaries in the ring lies below the critical value J_c . Since $J_c(T)$ decreases monotonically with increasing temperature, as the temperature is raised, a value $T = 87.9$ K is reached where flux begins to penetrate through the weaker of the two grain boundaries into the interior of the ring; this leads to a sharp break in both the real and imaginary parts of χ_{ac} (see vertical arrow in Fig. 2 (left)) at the kink temperature T_{kink} . As the temperature is increased further, additional flux penetrates into the center of the ring, but not through the superconducting material of the ring itself, until a plateau is reached above 90 K. Above 91.7 K magnetic flux begins to penetrate into the ring material until above 92 K all superconductivity has been destroyed and the flux distribution is uniform. These results from *ac* susceptibility measurements are in excellent agreement with parallel *dc* susceptibility measurements using a SQUID magnetometer on the same YBCO ring.

The shielding current I around the ring is directly proportional to the field amplitude H , $I = DH$, where, to a good approximation, D is the outer diameter of the ring [12]. In Fig. 2 (left) it is seen that under 0.6 GPa pressure T_{kink} shifts to higher temperatures, i.e. J_c at a given temperature increases. This means that under hydrostatic pressure the ability of the GB to carry current is enhanced. This result is confirmed by further studies at magnetic field amplitudes to ~ 23 G which suppress T_{kink} to temperatures below 20 K, as seen in Fig. 2 (right). In this figure the calculated values for J_c are given, where $J_c = I_c/A$ and A is the cross-sectional area of the ring. At all measured temperatures J_c is seen to increase rapidly with hydrostatic pressure at the rate +26 %/GPa which is much more rapid than that of T_c for the bulk material (~ 0.24 %/GPa).

We also find the change in J_c to be less if the pressure is varied at temperatures significantly below ambient; time dependences in J_c are also observed. Similar relaxation effects are well known in bulk YBCO where T_c is found to depend on the detailed pressure/temperature history of the sample [9, 10]. The extreme sensitivity of these relaxation effects on the oxygen content points to the mobile oxygen ions in the basal plane, the “chain layer”, as being their source. The bulk relaxation effects are smallest when the chain layer is fully developed and essentially all chain sites are filled, i.e. at the stoichiometry $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$. In analogy, the relaxation effects observed in J_c for the GB give evidence that the GB contains a sizeable number of oxygen vacancies, i.e. there’s room for more oxygen! If a way can be found to further enhance the oxygen concentration in the GB region, it is likely that higher values of J_c can be attained.

Further research is underway to determine the dependence of J_c on pressure as a function of both temperature and *dc* magnetic field over a wide range of oxygen content and misorientation angle θ [13].

3 Results on Alkali Metals

The nearly free electron picture works best for simple s, p -electron metals such as the alkali metals or noble metals. If a simple metal happens to be superconducting at ambient pressure (e.g. Pb, In, Sn, Al), T_c is invariably found to *decrease* under hydrostatic pressure. This result has a simple explanation [3]. According to the well-known McMillan formula, T_c depends exponentially on the electron-phonon coupling parameter $\lambda = \eta/\kappa$, where η is a purely electronic term, the Hopfield parameter, and $\kappa \equiv M \langle \omega^2 \rangle$ is a mean “spring constant” for the lattice. If λ decreases, so does T_c . The reason for the universal decrease in T_c under pressure for simple metals is that κ increases much more rapidly than does η . Another way to express this is that T_c decreases under pressure due to lattice stiffening. In transition metals the increase of η with pressure is comparable to that of κ , so that T_c may increase or decrease.

Since for simple-metal superconductors T_c always *decreases* under pressure, it would appear unlikely that a nonsuperconducting simple metal, like any of the alkali metals, would ever become superconducting under pressure. Over 30 years ago, however, Wittig [14] demonstrated that at pressures above 7 GPa the alkali metal Cs becomes superconducting near 1.5 K. At first glance this result would appear to contradict our above conclusions, but it does not. At pressures above 7 GPa Cs is no longer a simple metal! Near these pressures $s - d$ transfer occurs as the bottom of the $5d$ band drops below the top of the $6s$ band, thus turning Cs into a transition metal [15]. A similar scenario would be expected for the next lighter alkali metals Rb and K.

In this connection the alkali metal Li is of particular interest. Its unoccupied $3d$ band lies far above the Fermi energy; indeed, Li lies two rows up in the periodic table from the $3d$ transition metal series. In this picture, therefore, no pressure-induced superconductivity would be expected in Li, except at pressures well above the 100 GPa range. In 1986 Lin and Dunn [16] did report a possible phase transition in Li under quasihydrostatic pressures above 20 GPa, but the evidence for superconductivity was not unequivocal.

In 1998 Neaton and Ashcroft [17] made the alarming prediction that at sufficiently high pressures Li should cease to behave like a simple metal, but rather should show marked deviations from free-electron-like behavior. Because of core overlap the bands near E_f actually become narrower and band gaps increase markedly, thus contradicting basic high-pressure wisdom that under pressure bands broaden and band gaps decrease! This result was mentioned in an earlier paper by Boettger and Trickey [21]. At pressures sufficient to generate overlap of the Li-ion cores, the orthogonality requirements of the valence electrons to the core states leads to a marked enhancement in the pseudopotential and thus in the electron-lattice coupling. This in turn would be expected to generate structural phase transitions to lower symmetry structures and possible superconductivity. Extensive experimental [18, 19] and theoretical [20] investigations of structural phase changes in the alkali metals have confirmed these

general expectations. In 2001 Christensen and Novikov [22] predicted from *ab initio* electronic structure calculations that for *fcc* Li T_c would increase rapidly with pressure to values approaching 80 K. These predictions prompted several experimental groups to search in earnest for superconductivity in Li under pressure.

The first group to confirm a superconducting transition in Li was that of Shimizu *et al.* [23] in 2002 in a diamond-anvil cell experiment to 50 GPa. In their electrical resistivity measurement superconductivity appeared at 7.5 K for 30 GPa pressure, rising rapidly to values approaching 20 K; the pressure dependence $T_c(P)$ was combined from four separate experiments and exhibited considerable scatter. A few months later Struzhkin *et al.* [24] measured the *ac* susceptibility to 40 GPa and the resistivity to 82 GPa, reporting an onset of superconducting at 10 K for 23 GPa with a rapid rise under pressure to ~ 16 K at 35 GPa.

In both these studies no pressure medium was used, the diamond anvils being allowed to press directly onto the Li sample. This raises the question whether shear stresses on the Li in such experiments may have played a role in the reported superconducting transition. Such effects have been well documented. In the first high-pressure ever carried out on a superconductor, Sizoo and Onnes [1] reported for both Sn and In that T_c decreased under hydrostatic pressure, but *increased* if uniaxial pressure was applied. If Li metal is cooled from ambient temperature, it undergoes a martensitic phase transformation at $T_{pt} \simeq 75$ K from the *bcc* to a *Rh6* low-temperature phase. Under hydrostatic pressure T_{pt} increases at the rate +30 K/GPa [25], but under uniaxial pressure $dT_{pt}/dP \simeq +1250$ K/GPa [26], a rate 40 \times faster! In the present experiment, in fact, nonhydrostatic shear stresses on the Re gasket resulted in a sharp increase in Re's superconducting transition temperature to 3.5 K, thus preventing the detection of superconductivity from the Li sample at lower temperatures. Further examples of sharply differing hydrostatic versus uniaxial pressure effects on superconductivity are given in Ref. [27]. For this reason we set out to search for superconductivity in Li using the most hydrostatic pressure medium of all, dense He.

In Fig. 3 (left) we show the coil arrangement we used for *ac* susceptibility measurements in our nonmagnetic BeCu diamond-anvil cell. Two identical coils are shown wound with 60 μm Cu wire consisting of an outer primary coil (130 turns) and an inner secondary coil (180 turns). One coil is placed around the lower diamond anvil (1/6 carat, 0.5 mm culet) with the compensating coil directly adjacent. Both coils and lead wires are thermally anchored to an insulating board with GE varnish. A preindented Re gasket is placed in both measuring and compensating coils to reduce the background signal in the *ac* susceptibility. Before applying pressure, liquid He is filled into the gasket hole to serve as a nearly hydrostatic pressure medium. Further experimental details are given in Ref. [27].

In Fig. 4 we show the superconducting phase diagram for Li metal under nearly hydrostatic pressures to 67 GPa [27]; this diagram differs significantly from the results of the previous studies[16, 23, 24], particularly above 30 GPa. In the first run 25 data points were obtained as a function of both increasing and decreasing pressure. We

find that under nearly hydrostatic pressure Li becomes superconducting at ~ 5 K for 20 GPa, T_c increasing initially rapidly with pressure to ~ 14 K at 30 GPa. At this pressure a structural phase transition appears to occur as evidenced by the sharp break in slope dT_c/dP . At higher pressures $T_c(P)$ passes through a minimum before dropping below 4 K at 67 GPa. Although it is possible that at or above 67 GPa Li has transformed into the paired semiconducting/insulating state envisioned by Neaton and Ashcroft, we have no clear evidence for this. At 67 GPa our Li sample remains opaque to transmitted light in the visible region; from this one can infer that Li is either still a metal or a semiconductor with a band gap less than 1.7 eV. A more complete discussion of these results, including evidence that Li is a type I superconductor, is given in Ref. [27].

Following the experiments on Li metal, two further alkali metals, Na and K, were subjected to nearly hydrostatic dense He pressure in a search for superconductivity. Shi *et al.* [28] have carried out an electronic structure calculation on K and Rb and predict an onset of superconducting near 13 GPa for K and 8 GPa for Rb with a rapid rise in T_c with pressure, in analogy with Li. In our experiment on Na metal to 65 GPa, however, no superconducting transition could be detected above 4 K. K metal also failed to become superconducting above 4 K to 43.5 GPa pressure. In a second experiment on K a nonsuperconducting MoW gasket was used which permitted measurements to lower temperatures. In this experiment no superconductivity was detected in K above 1.5 K to 35 GPa pressure. In a quasihydrostatic experiment to 21 GPa by Ullrich *et al.* [29], no superconductivity was found in Rb above 0.05 K.

It would seem almost certain that all alkali metals will become superconducting under sufficient pressure; after all, both the lightest (Li) and heaviest (Cs) alkali metals do become superconducting! Further experiments are underway over expanded temperature/pressure ranges to search for superconductivity in Na, K, and Rb.

Acknowledgments. The authors are grateful to N.W. Ashcroft and J.B. Neaton for stimulating discussions. Research is supported by NSF Grant No. DMR-0404505.

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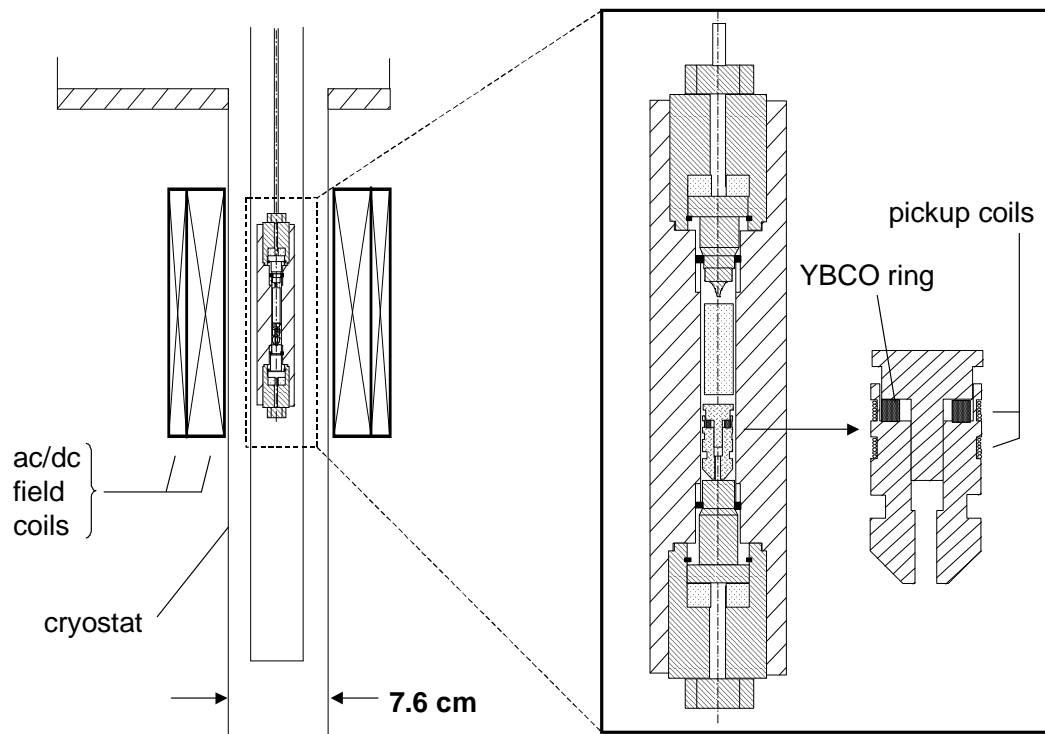


Figure 1. Sample holder on right fits inside 7 mm bore of He-gas pressure cell which is inserted in closed-cycle refrigerator.

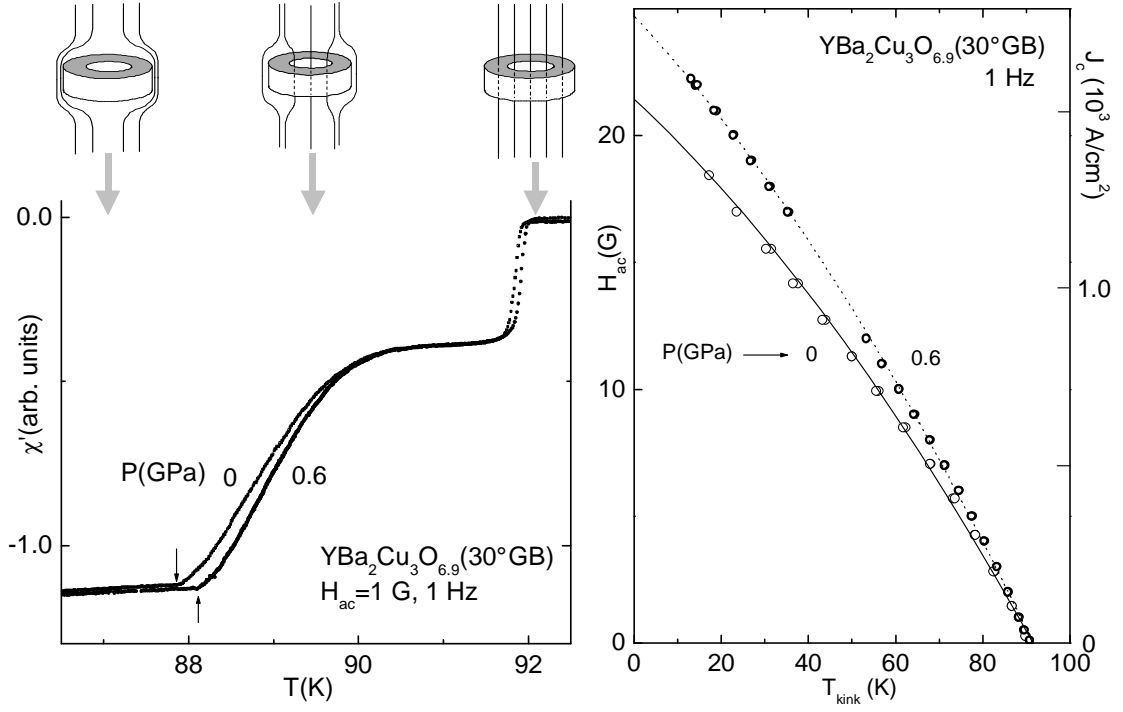


Figure 2. (left) real part of ac susceptibility versus temperature for YBCO ring at two different pressures. (right) *ac* field amplitude versus kink temperature at two different pressures.

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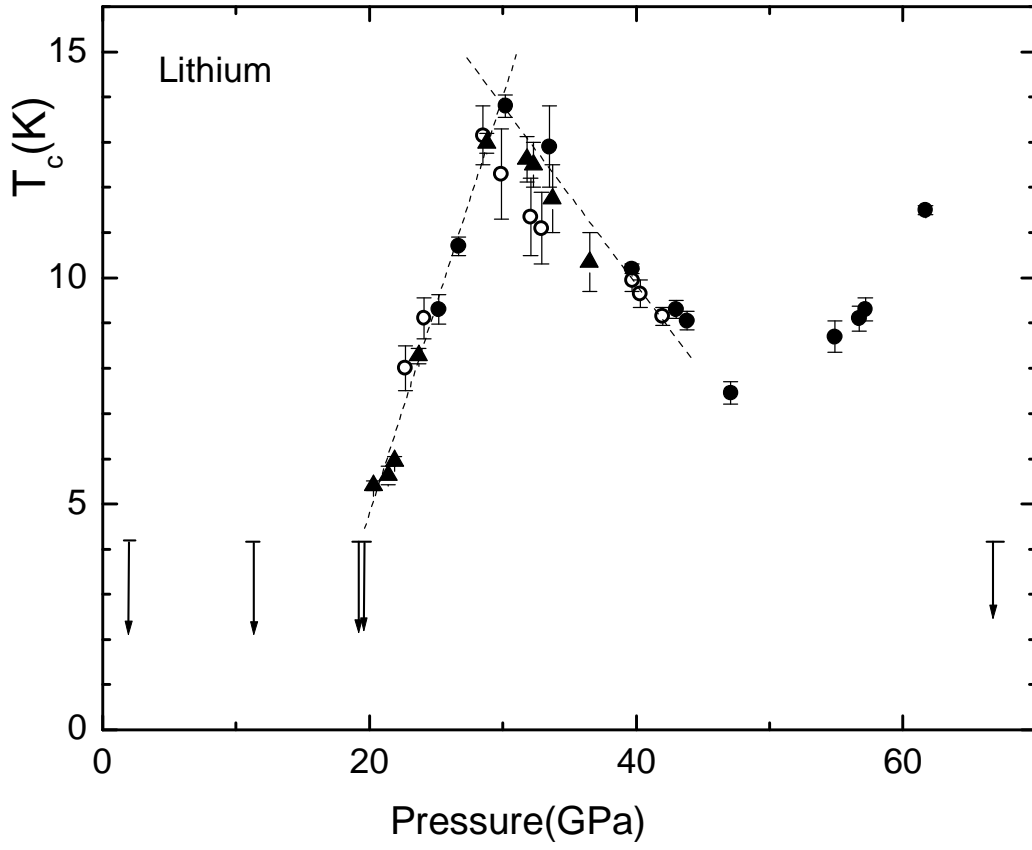


Figure 4. Superconducting phase diagram of Li metal under nearly hydrostatic pressure: run 1 increasing pressure (\bullet), run 1 decreasing pressure (\circ), run 2 increasing pressure (\blacktriangle).